XRD Unit-2 (Second part)

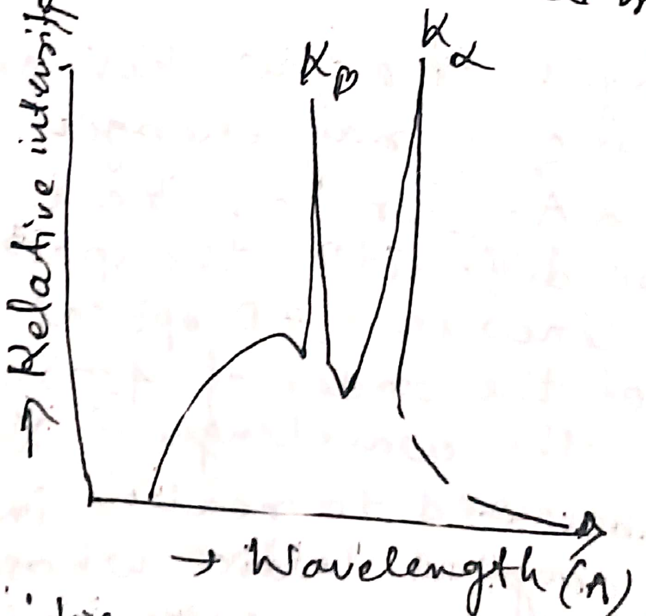
(XRD is an experimental technique used to determine the crystal structure and lattice parameters of material systems in bulk and nanoregimes.)

Typical interatomic distances in a solid are of the order of few Angstroms ($1\mathring{A} = 10^{-10}$ m $= 0.1$ nm). An electromagnetic (EM) probe of the microscopic structure of a solid, should have a matching wavelength corresponding to the energy of the order of $E = h\nu = \frac{hc}{\lambda} = \frac{hc}{10^{-10}}$

$= 12.3 \times 10^3$ eV.

Energies of a few KeV produce characteristic X-ray energies of wavelength $\sim 1-2\mathring{A}$. [For visible e.m. radiation to be diffracted, the spacing between the lines in a 2D optical grating should be of the order of 4000–7000 Å. Therefore, the wavelength of X-rays $\lambda_{x\text{-}ray} \sim 1-2\mathring{A}$ can be used to realize information about the crystal lattice whose dimensions are in the same range as this wavelength range.]

The X-rays emitted by source made of certain heavy elements (Mo, Cu, Co, Fe, Cr and Zn) consist of a continuous wavelength range (which is termed as white radiation or Bremsstrahlung). The minimum wavelength in the continuous wavelength (λ) spectrum is inversely proportional to the applied voltage that accelerates the electrons towards the target. If the applied voltage is sufficiently high, then in addition to the radiation continuum, a characteristic radiation of a specific wavelength and intensity is also emitted by the target.



Characteristic spectrum of X-rays emitted from a Mo target at 35 Kev.

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X-ray diffraction (XRD) is based on constructive interference of diffracted rays by the atoms or ions of the sample from successive lattice planes, which satisfy condition of Bragg's law

$$2d\sin\theta = n\lambda$$

where d = interatomic separation between the lattice planes,

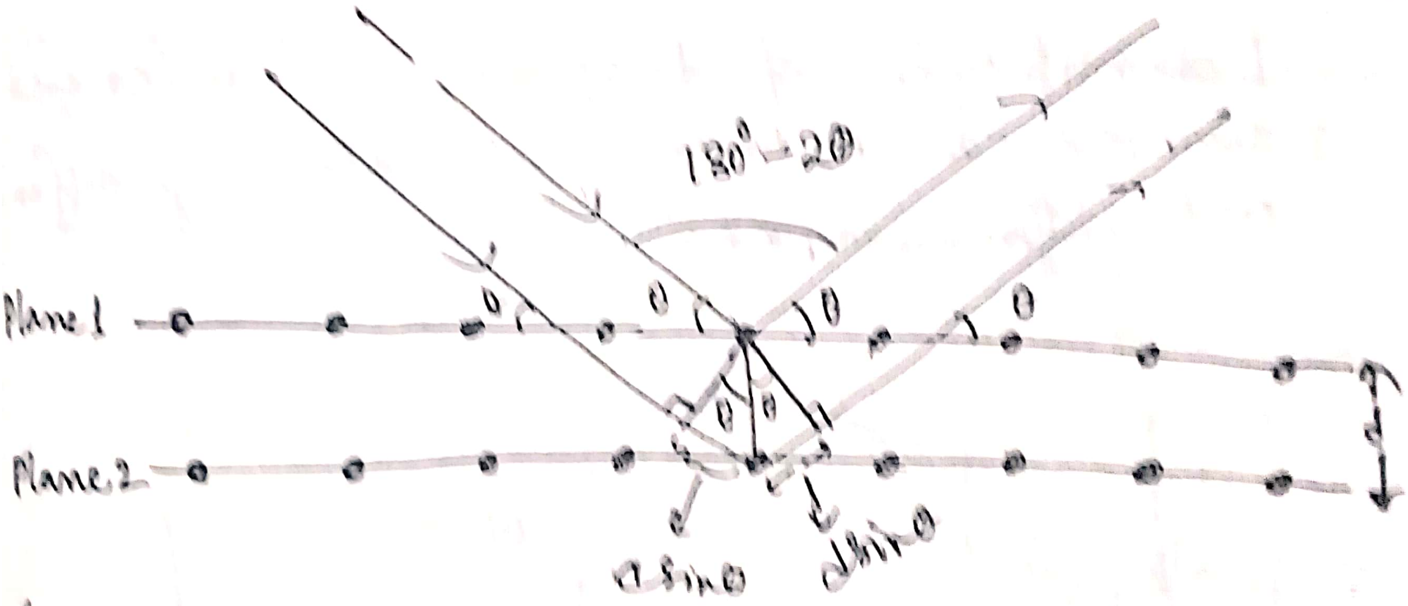

Fig :- X-rays shown specularly diffracted from adjoining planes.

N.B. Very small λ [λ ~ 0.1 Å] produces no reflection, it leads to absorption in the prism.

This law relates the wavelength of X-ray to diffraction angle and lattice spacing in sample. These diffracted X-rays are detected, processed and counted. scanning the sample through a range 2θ angles, all possible diffracted times rays can be captured due to random orientation of powder material.

Identification of d-spacing of different sample can be done by analysing different diffraction peak.

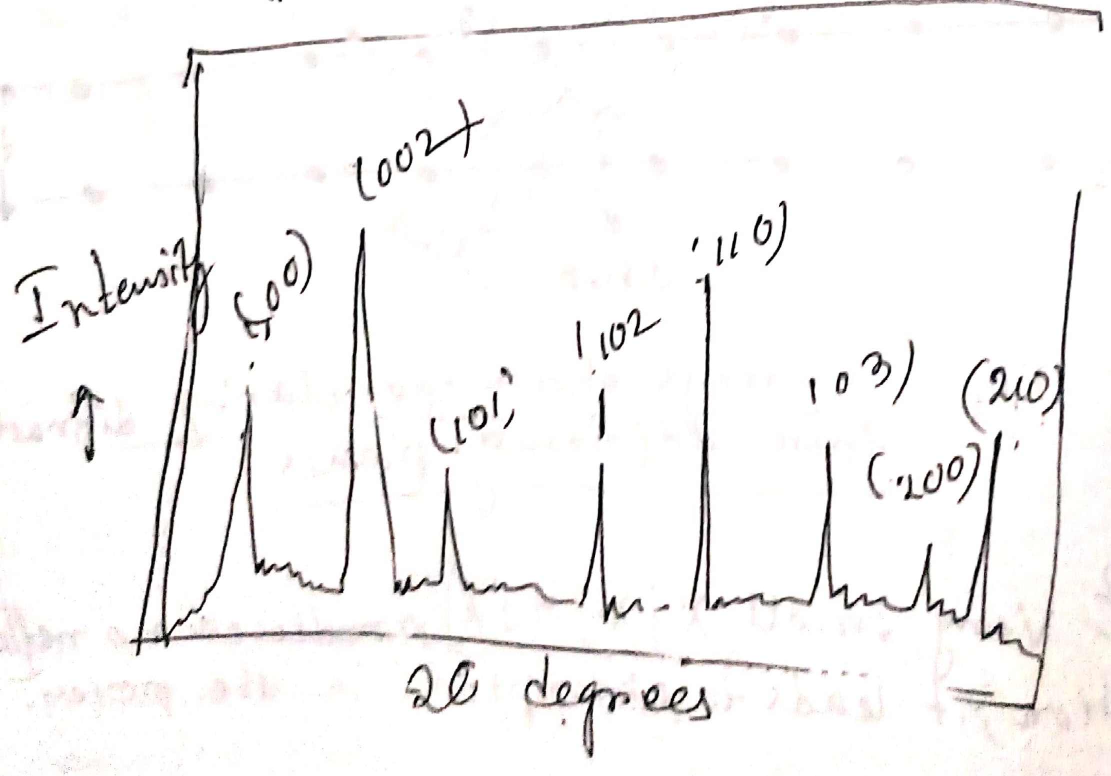

fig. shows XRD pattern which indicates random orientation of particles/crystallites in a polycrystalline material.

Structural changes in nanomaterials

...e known to contain a large number of small single crystallites with random orientation. In the case of nanoparticles, the particles also have random orientation e.g. In case of gold nanoparticles, the structural properties evolve with size and ~~size~~ shape,

XRD is based on wide-angle elastic scattering of X rays. Since grain size in nano-particles is very small, the diffraction pattern of nanoparticles looks similar to those of amorphous substances.

Single crystal nanoparticles exhibit size dependent features including slight shifts in the position of Bragg peaks, anomalous peak heights and widths. The peaks show considerable broadening for nanophase materials (particles, clusters, quantum dots etc). The diffraction peaks for well-crystallized materials are very sharp, but for most of the polycrystalline materials, the peaks are broad.

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The empirical formula for obtaining the crystalline size is given by

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where λ is the wavelength, β gives Broadening of diffraction line measured at half its maximum intensity in radians and D is the average crystal size. Line broadening is mainly used to measure the particle size of free flowing powders.

To find out the parameter β, we mix the material with a standard sample that has a particle size greater than 100 nm. In the diffraction pattern of this mixture, we obtain sharp line from the standard and broad lines from the test sample. If β_s is the broadening for the standard, β_M is of the material then β is given by

$$\beta^2 = \beta_M^2 - \beta_s^2$$

Another method for determining the particle sizes of nanoparticles. It comes from the diffuse scattering close to the transmitted beam. It helps in size as well as shape determination of amorphous and crystalline materials

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SEM

[S]canning electron Microscopy

[SE]M is an analytical instrument which [res]olution is less than 1 nm. It is used to [st]udy topography, morphology, composition [an]d crystallographic information.

[S]EM is a type of electron microscope capable of producing high resolution images of a sample surface. Whole system of SEM must be vacuum protected to prevent scattering of the electrons by stray air molecules and the speciman must absorb or reflect electron

SEM consists of virtual source at the top represents the electron gun, producing a stream of monochromatic electrons. The stream is then condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to ~~both~~ form the beam and also to limit the amount of current in the beam. It works in conjunction with the condenser aperture (not user selectable) to eliminate the high angle electrons from the beam. The beam is then constricted by the condenser aperture eliminating some high angle electron.

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The 2nd condenser lens forms the elect into a thin, tight, coherent beam and usually controlled by the "fine probe current knob." A user selectable objective aperture further eliminates angle electrons from the beam. A se coils then scan and sweep the beam a grid fashion dwelling on points for period of time determined by the sca speed (microsecond range). The final le the objective, focuses the scanning bea onto the part of the specimen desired when the beam strikes the sample and dw for a few microseconds) interaction occ inside the sample and are detected wit various instruments. Before the bea moves to its next dwell point, these in truments count the number of interact and display a pixel on a CRT whose inte sity is determined by this number (th more the reactions, the brighter the pixel This process is repeated until grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.

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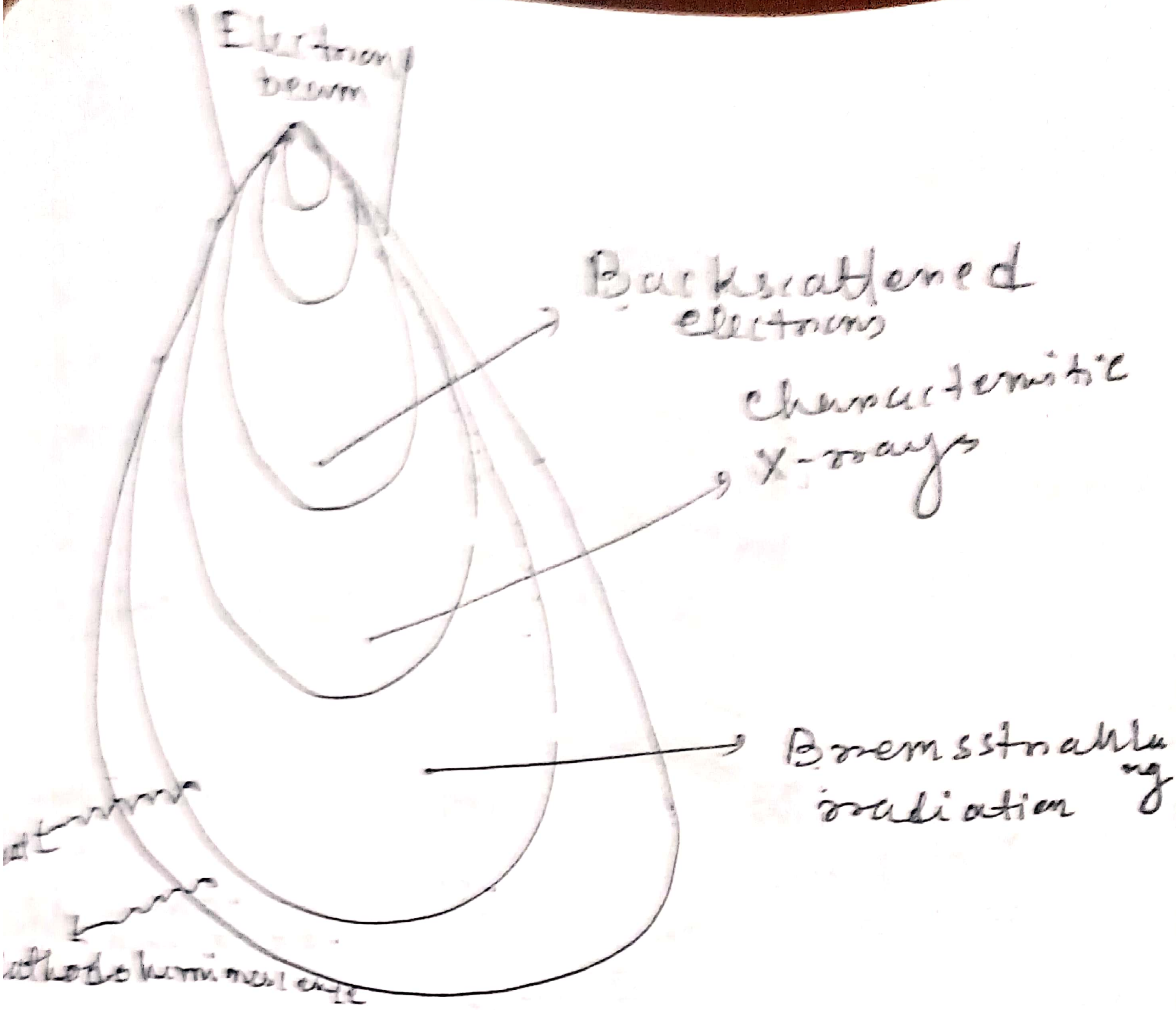
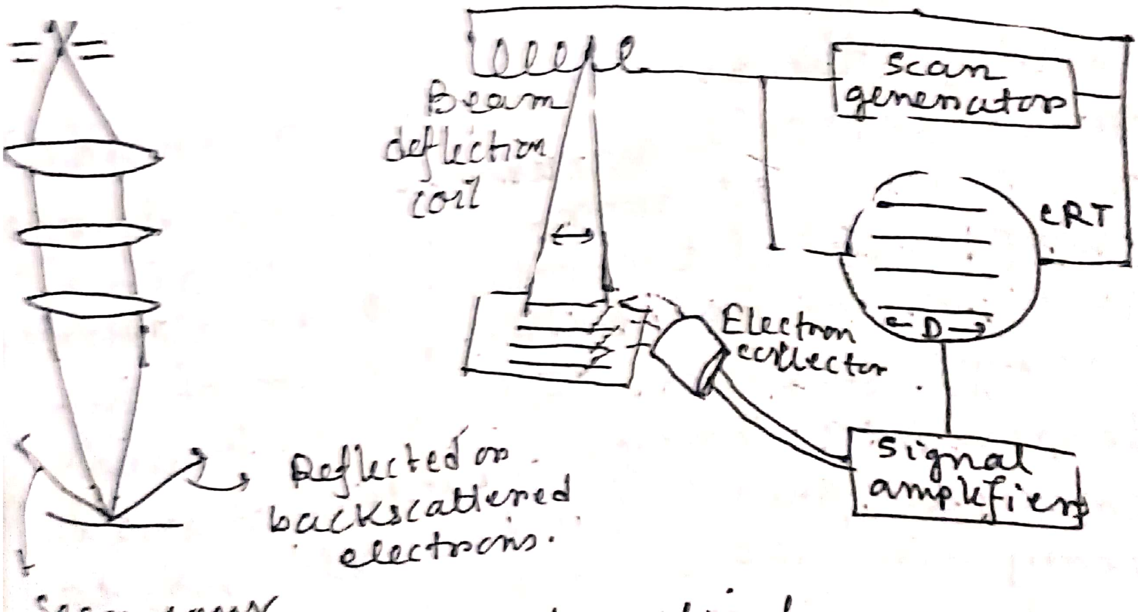
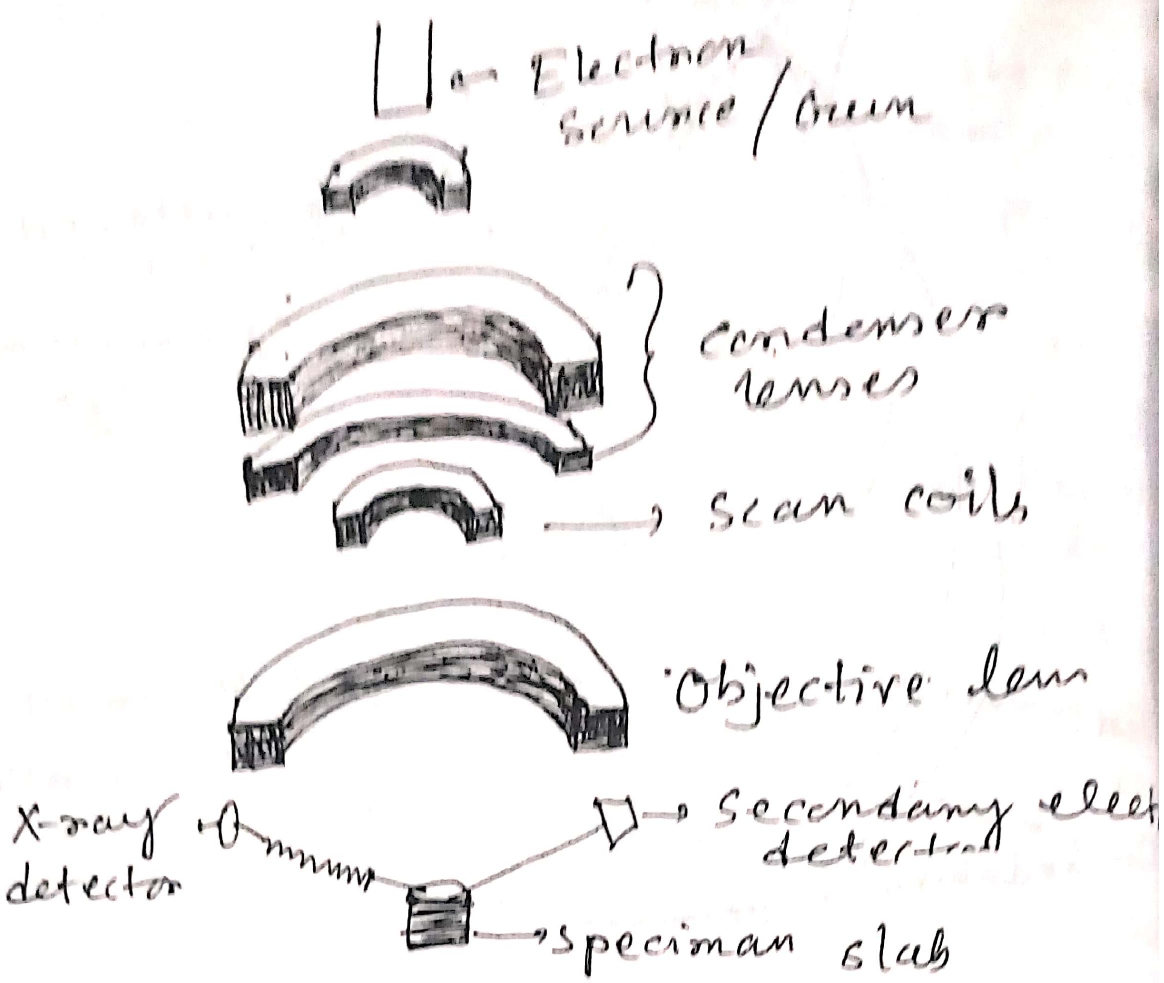


schematic of electron interaction with matter



schematic of a SEM and the electronics involved



Schematic diagram of SEM

Firstly, the sample is placed inside microscope's vacuum column through an air-tight door. After the air is pumped out of the columns, an electron gun (at the top) emits a beam of high energy electrons. This beam travels downward through a series of magnetic lenses designed to focus the electrons to a very fine spot. Near the bottom, a set of scanning coils moves the focused beam back and forth across the speciman row by

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As the electron beam hits each spot
u ~~spo~~ sample, secondary electrons
nocked loose from its surface. A
tor counts these electrons and sends
ignals to an amplifier. The final image
uilt up from the number of electrons
tted from each spot on the sample.

What is the advantages of FESEM
er Normal SEM?

⇒ In Normal SEM, electrons are
hermionically emitted from a
ilament based cathode and are accelerat-
d towards an anode.

In FESEM, electrons can be emitted
via field emission. A cold cathode
field emitter, ~~does~~ is used which
does not require to heat the filament.

FESEM produces clearer, less electro-
statically distorted images with high
spatial resolution down to 1 nm. This is
3 to 6 times better than conventional SEM

Also in FESEM, smaller area con
mination spots can be examined
electron accelerating voltages. A
result high quality, low voltag
images are obtained with negligi
electrical changing of samples.

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AFM

=) mesures topography (hight, roughness)

The instrument is based on the princi- that when a tip is integrated to the [e]nd of a spring cantilever, is brought with[in] the interatomic separation between [th]e tip and the sample, interatomic po[t]entials are ~~dele~~ developed between the [a]toms of the tip and the atoms of the [s]urface. As the tip moves across the [s]urface, the interatomic potentials force [t]he cantilever to bounch up and down [w]ith the change in contours of the surface. Therefore by measuring the deflection of the cantilever, the topographic features of the surface can be mapped out.

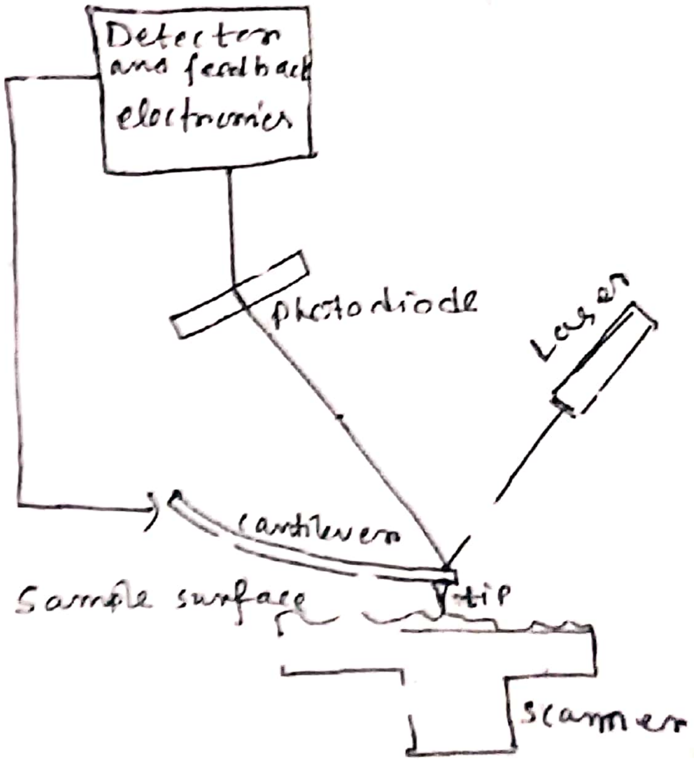
The measured cantilever deflection in AFM apparatus can be detected using a laser beam that is focused on the backside of the reflective coated canti-lever and the reflected laser beam intensity is measured using a photo sensitive diode (split photo diode) that in turn allows a computer to generate a map of surface corrugations or morphology or topography.

So ~~In~~ AFM operates by measuring attr
or repulsive forces betⁿ a tip and the sam

* In repulsive contact mode, a large lateral force can be exerted on the sample as the tip attached at the end of leaf spring or cantilever is drag over the specimen and some sort of deflection measuring apparatus measure the vertical deflection of the cantilever which indicates the local sample heig But the forces can ~~deform~~ result in deformation of images and damaging sample. This type of microscopy is also called lateral force microscop (CLFM)

* In Tapping mode or non contact mode, AFM derives topographic image from measurements of attractive forces Here the tip is not in ~~in~~ constant contac with the surface, the tip makes intermi ttent contact with the surface. As the tip scanned over the surface, the cantilever is driven at resonant freq. (hundreds of KHz).

because the contact time is a small fraction of its oscillation period and hence the lateral forces can be reduced dramatically. Tapping mode is usually preferred to image samples with structures that are weakly bound to the surface on samples (polymers, thin films). There are also two types of image contrast mechanisms in tapping mode → one is Amplitude imaging and another is phase imaging. In amplitude imaging, the feedback loop adjusts the Z-piezo so that the amplitude of the cantilever oscillation remains constant. The voltage needed to keep the amplitude constant can be compiled into an image



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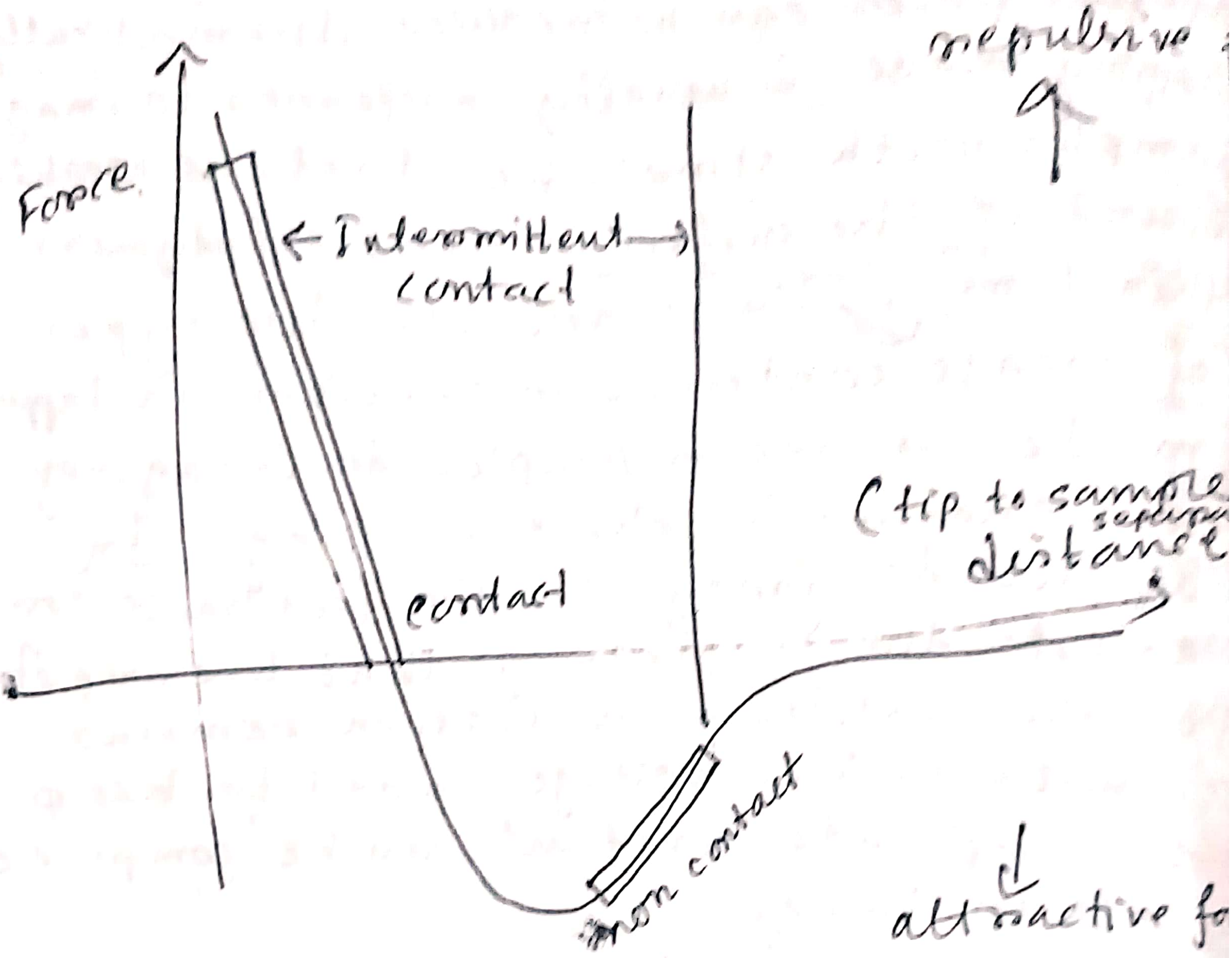
Schematic diagram of the operating principle of an AFM

force distance curve



Lithographic process → p-110

Ball milling → p-161 Rao 136

Advantages and disadvantages of top-down and Bottom up approach.

\# Chemical vapor deposition (CVD) :- A process where ~~by~~ a thin solid film is deposited on-to a substrate through chemical reaction of the Gaseous species ~~of~~ ⇒ ...

\# p-113 Physical vapour deposition (PVD) is a physical process ⇒ where atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions usually or commonly used for thin film deposition. The process is of driven by momentum exchange between the ions (non-reactive ions like Ar) and atoms in the material, due to collisions.

(e.g → sputtering). A glow-discharge (plasma) of non-reactive ions (Ar) is created by a potential difference inside a vacuum chamber, which fall on the target (the material to be deposited) and break ✱